Electronic Supplementary Material (ESI) for Dalton Transactions

Chemistry of Transition Metal Carbene Complexes [7]: Nucleophilic Substitution Reactions of Cyanamide Anion to Fischer Carbene Complexes: Kinetics and Computational Studies

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Table S1. Details of solution preparation and observed pH values.

Sl no.	$[N{\equiv}C\text{-}NH_2]_t$/M	[KOH]/M	$[N{\equiv}C\text{-}NH_2]$/M	$[N{\equiv}C\text{-}NH^-]$/M	$[N{\equiv}C\text{-}NH^-]/[N{\equiv}C\text{-}NH_2]$/	pH_{obs}
1	0.10	0.01	0.09	0.01	0.11	10.41
2	0.10	0.02	0.08	0.02	0.25	10.77
3	0.10	0.03	0.07	0.03	0.43	11.00
4	0.10	0.04	0.06	0.04	0.67	11.20
5	0.10	0.05	0.05	0.05	1.00	11.37
6	0.10	0.06	0.04	0.06	1.50	11.55
7	0.10	0.07	0.03	0.07	2.33	11.74
8	0.10	0.08	0.02	0.08	4.00	11.97
9	0.10	0.09	0.01	0.09	9.00	12.32

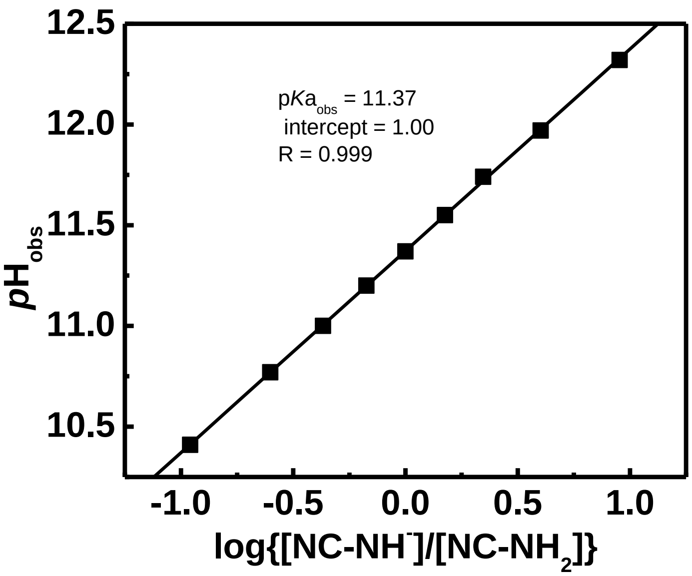

Figure S1(a). Plot of pH_{obs} vs. log{$[N{\equiv}C{-}NH^-]$/$[N{\equiv}C{-}NH_2]$}

Synthesis of Cr-NHCN-OMe. As a representative one we have prepared **Cr-NHCN-OMe** as follows: 0.171 g (0.5 mmol) of **Cr-OMe-OMe** was dissolved in 20 mL acetonitrile in a round bottom flak under Ar atmosphere. To this solution 2 mmol of N≡C-NHK in 15 mL acetonitrile was added; the latter was prepared by reacting cyanamide with one equivalent of KOH dissolved in a minimum volume of water. The mixture was allowed to react for one hour whereupon the solvent was removed under high vacuum. The oily product was dissolved in a minimum volume of 50% MeCN-50% CH_2Cl_2 (v/v) and charged on a silicagel column prepared with the same solvent mixture. The yellow band was collected and dried under high vacuum.^{1}H NMR (Bruker,500 MHz) δ ($CDCl_3$): 3.66 (CH_3O), 4.1 (NH), 7.02 -7.70 (C_6H_4). ES-MS$^+$: (352)

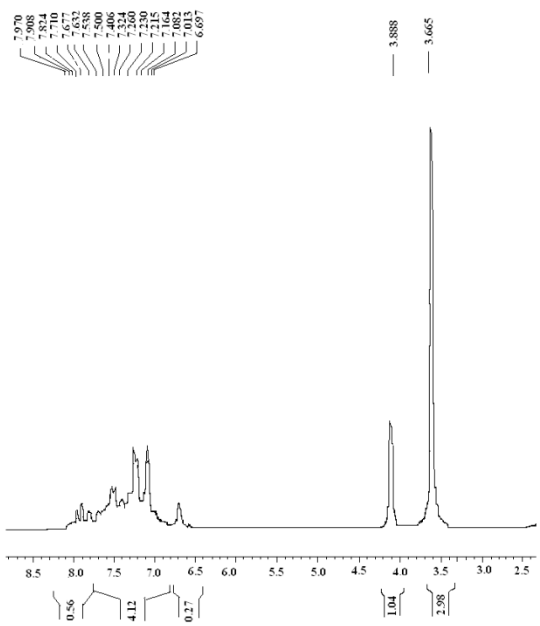

Figure S1(b). ^{1}H NMR spectrum of Cr-NHCN-OMe in $CDCl_3$ (Bruker 500 MHz).

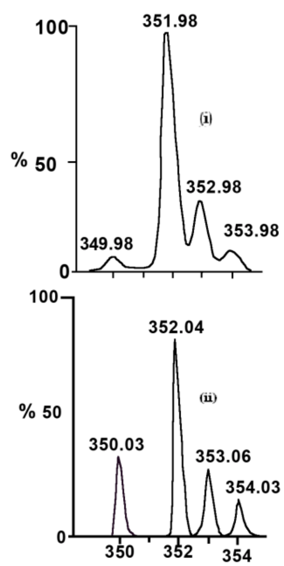

Figure S1(c). ESI-MS$^+$ of Cr-NHCN-OMe. (i) simulated spectra, (ii) Experimental one

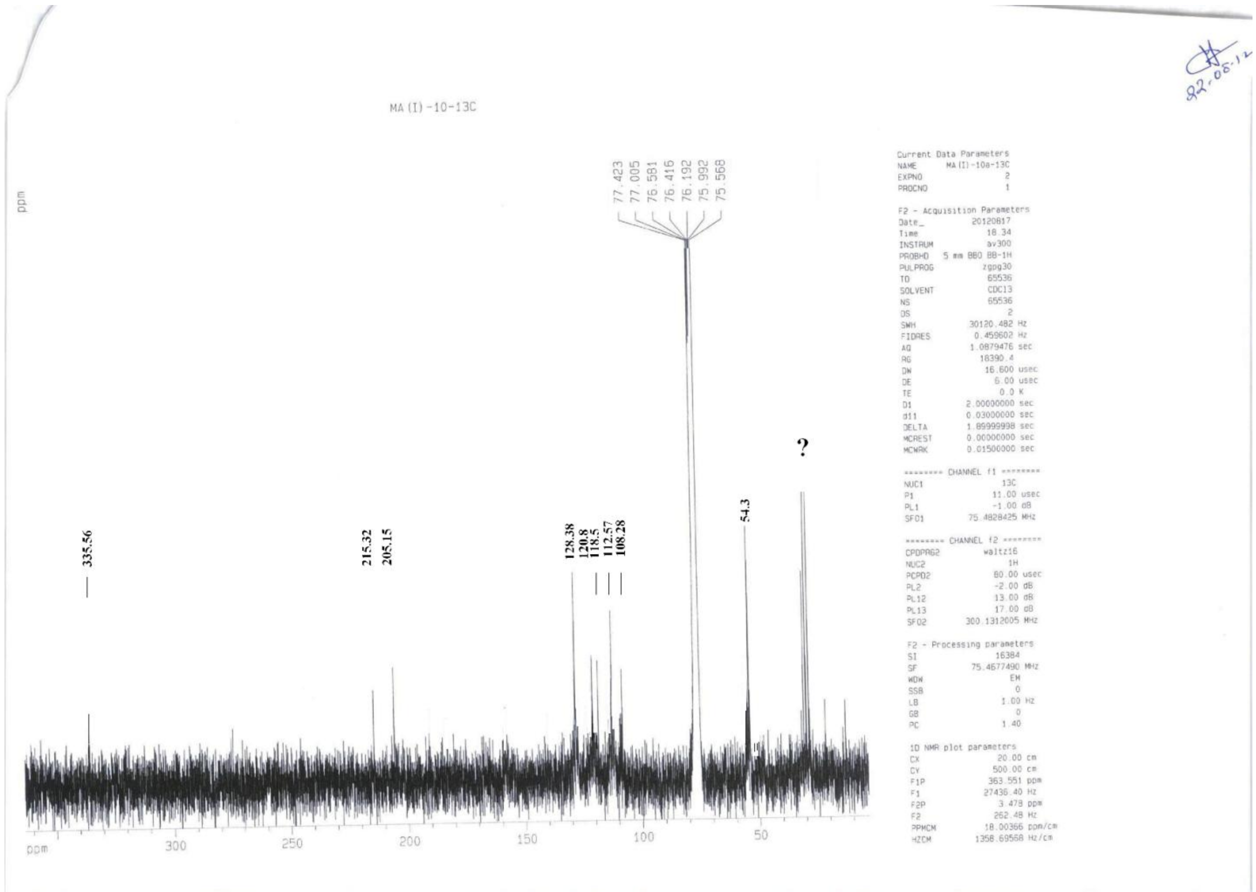

Figure S1(d). ^{13}C-NMR spectrum of Cr-NHCN-OMe in $CDCl_3$

Table S2(a). Summary of pseudo-first-order rate coinstants (k_{obs}, s-1) for the reaction between **Cr-SMe-Z** (Z = *p*-CF_3, *p*-Cl and *m*-Cl) as a function of pH in 50% H_2O-50% MeCN. Conditions are: [C] = 5.0x10^{-5} M, [H_2N-CN]$_t$ = 0.20 M, T= 25 °C.

pH	[H+]/M	K_{obs}(Cr-SMe-CF_3)	K_{obs}(Cr-SMe-m-Cl)	K_{obs}(Cr-SMe-p-Cl)	K_{obs}(Cr-SMe-p-F)	K_{obs}(Cr-SMe-p-Me)	K_{obs}(Cr-SMe-p-OMe)
10.66	2.19e-11	0.41	0.24	0.23	0.17	0.07	0.07
11.05	8.91e-012	0.98	0.52	0.52	0.33	0.15	0.15
11.34	4.57e-012	1.75	0.74	0.64	0.52	0.22	0.17
11.56	2.75E-12	2.15	1.11	1.23	0.72	0.29	0.23
11.76	1.74e-12	3.10	1.73	1.66	1.06	0.36	0.30
11.96	1.10E-12	3.69	2.09	2.20	1.32	0.42	0.33
12.14	7.24E-12	4.23	2.45	2.54	1.80	0.49	0.45
12.46	3.47e-13	4.50	3.45	3.11	2.50	0.56	0.47
12.77	1.70e-013	4.90	3.95	3.65	2.90	0.63	0.52
k_1/$M^{-1}s^{-1}$ → K_a^{NH} →		**26.8±0.70** **(2.19±0.07)x10^{-12}**	23.48±0.67 (0.895±0.07)x10^{-12}	**20.8±0.56** **(1.26±0.08)x10^{-12}**	**18.20±0.70** **(0.70±0.05)x10^{-12}**	**3.29±0.07** **(2.18±0.14)x10^{-12}**	**2.27±0.14** **(2.12±0.34)x10^{-12}**

Table S2(b). Summar of pseudo-first-order rate coinstants for the reaction between **M-SMe-H** (M Cr and W) as a function of pH in 50% H_2O-50% MeCN. Conditions are: [C] = 5.0x10^{-5} M, [H_2N-CN]$_t$ = 0.05 M, T= 25 °C.

pH	[H+]/M	k_{obs}(Cr-SMe-H)/s^{-1}	k_{obs}(W-SMe-H)/s^{-1}
10.52	3.02E-11	0.043	0.19
10.93	1.17E-11	0.059	0.41
11.17	6.76E-12	0.146	0.63
11.37	4.27E-12	0.195	0.84
11.55	2.82E-12	0.252	1.04
11.74	1.82E-12	0.305	1.24
11.94	1.15E-12	0.346	1.43
12.20	6.31E-13	0.399	1.66
12.51	3.09E-13	0.463	1.84
k_1→ K_a→		40.24±0.27 $M^{-1}s^{-1}$ (2.98±0.06)x 10^{-12}	10.26±0.33 $M^{-1}s^{-1}$ (2.52±0.23)x 10^{-12}

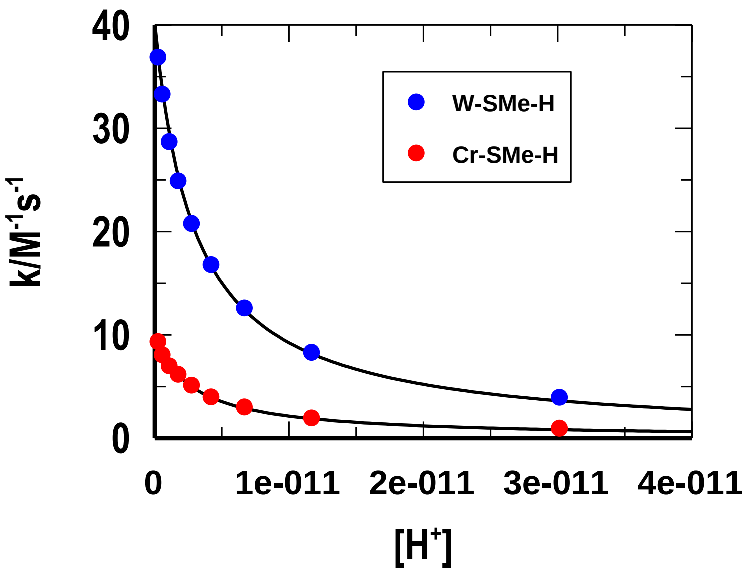

Figure S2(a). Plots of k ($M^{-1}s^{-1}$) vs. [H^+] for the reaction of W-XMe-H (X = O and S) with N≡C-NH^- at different pH in 50%MeCN-50% H_2O. Conditions are: [C] = 5.0 x 10^{-5} M, [NH_2-CN] =0.05 M and temperature 25 °C

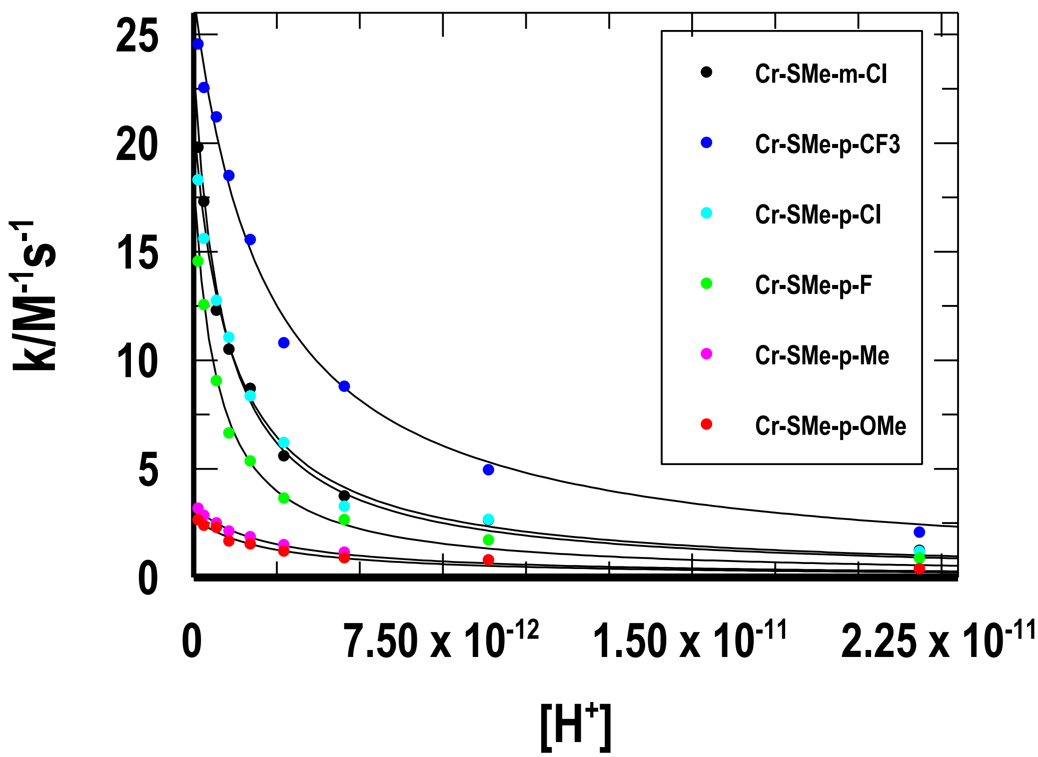

Figure S2(b) . Plot of k vs. [H^+] for the reaction of NC-NH^- with **Cr-SMe-Z** in 50% H_2O-50% MeCN at different pH. Conditions are: [C] = 5.0x10^{-5} M, [H_2N-CN]$_t$ = 0.20 M, T= 25 °C.

Table S3(a). Summary of Data for the reaction between **Cr-OMe-NMe₂** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	$k_{obs}{}^1$/s^{-1}(Cr-OMe-*p*-NMe_2))
0.005	0.0079
0.015	0.021
0.025	0.04
0.035	0.059
0.05	0.086
1.00E-01	0.159

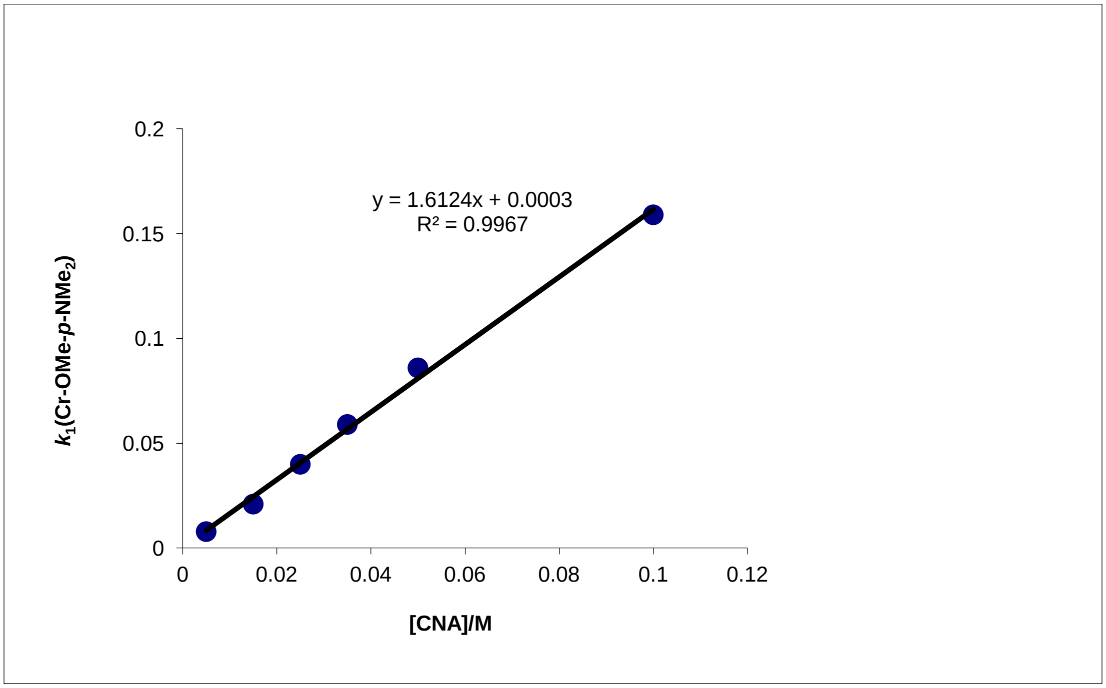

Figure S3(a). Plot of $k^1{}_{obs}$ vs. [N≡C–NH⁻] for the reaction between **Cr-OMe-NMe₂** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(b). Summary of Data for the reaction between **Cr-OMe-OMe** with N≡C–NH^{-} in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	$k_{obs}{}^{1}$/s^{-1}(Cr-OMe-OMe))
0.005	0.639
0.015	1.39
0.025	2.39
0.035	3.28
0.05	5.14
1.00E-01	8.94

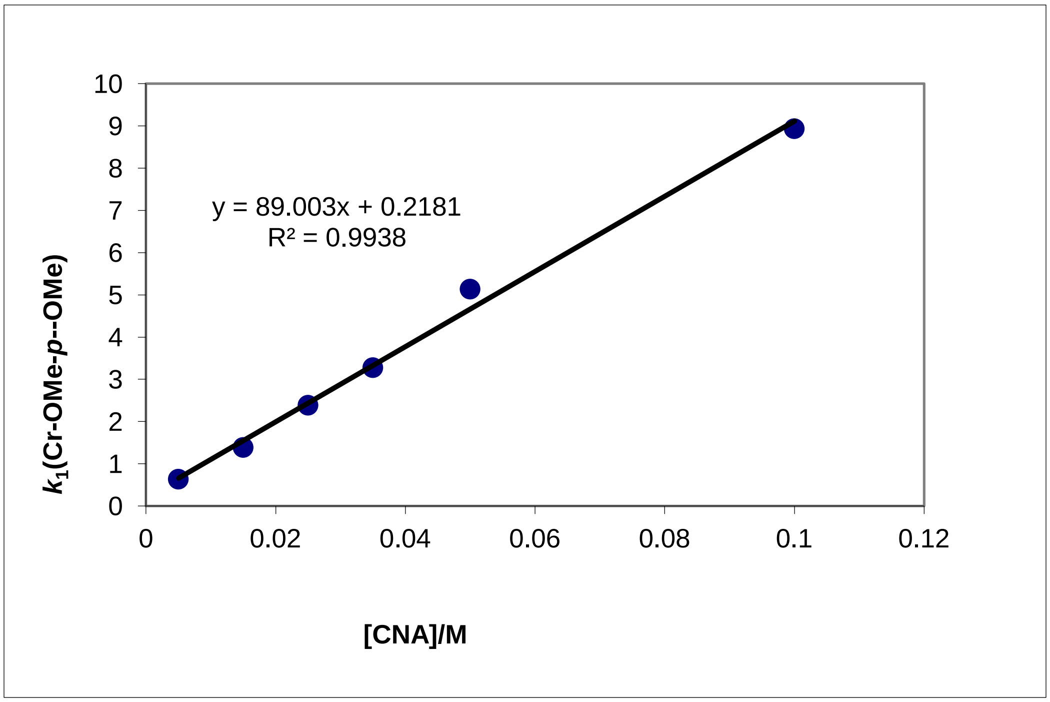

Figure S3(b). Plot of k^{1}_{obs} vs. [N≡C–NH^{-}] for the reaction between **Cr-OMe-OMe** with N≡C–NH^{-} in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(c). Summary of Data for the reaction between **Cr-OMe-H** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	k_{obs}^{1}/s^{-1}(**Cr-OMe-H**)
0.025	16.640
0.035	23.600
0.050	28.500
0.063	36.300
0.075	39.600
0.088	49.400
0.100	58.000

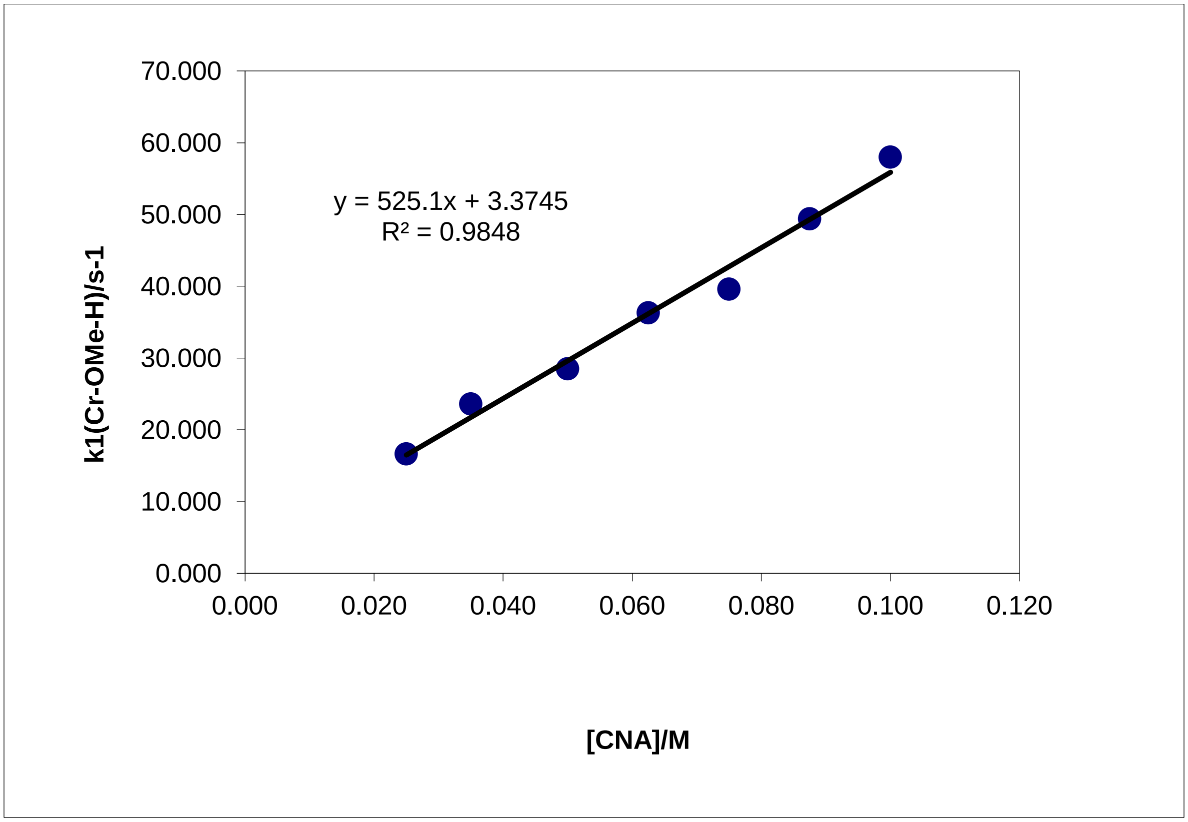

Figure S3(c). Plot of k^{1}_{obs} vs. [N≡C–NH⁻] for the reaction between **Cr-OMe-H** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(d). Summary of Data for the reaction between **Cr-OMe-*p*-F** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	$k_{obs}{}^1$/s^{-1}(Cr-OMe-*p*-F)
0.01	9.80
0.02	16.90
0.03	32.80
0.04	40.90
0.05	55.90
0.10	100.00

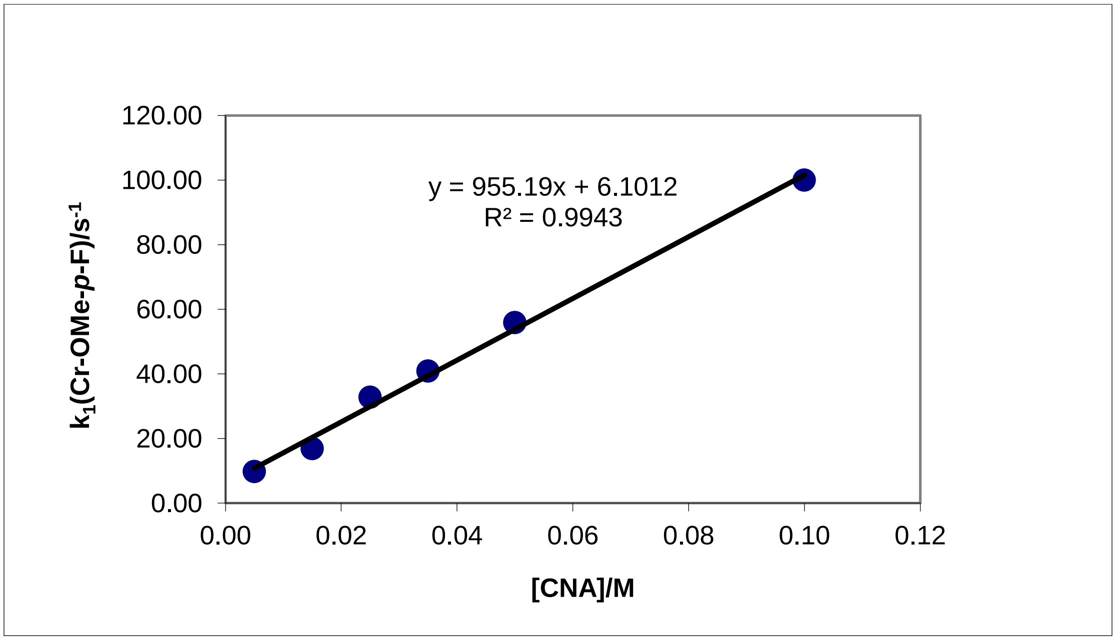

Figure S3(d). Plot of k^1_{obs} vs. [N≡C–NH⁻] for the reaction between **Cr-OMe-*p*-F** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(e). Summary of Data for the reaction between **Cr-OMe-*p*-Cl** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C

[CAN]/M	k_{obs}^{I} /s^{-1}(Cl)
0.005	17.8
0.015	36.9
0.025	65.0
0.035	96.0
0.050	118.0
0.100	230.0

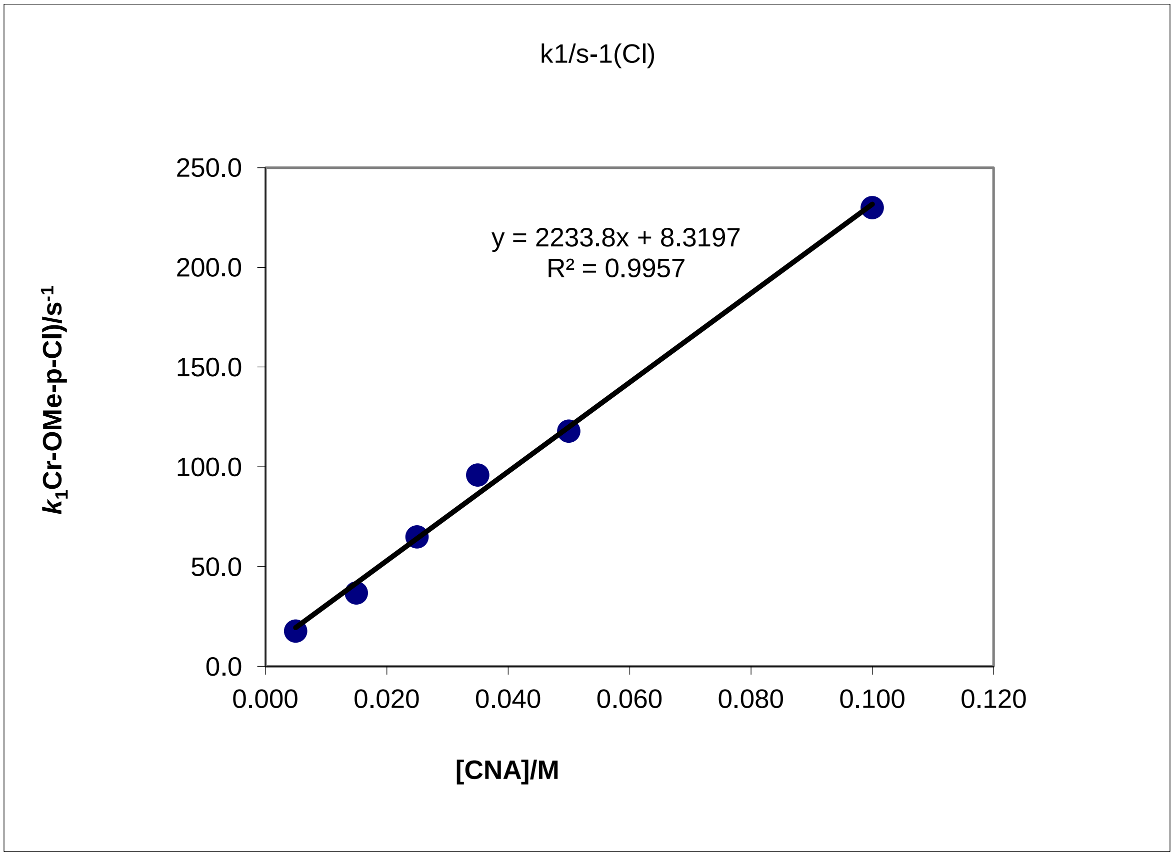

Figure S3(e). Plot of k_{obs}^{1} vs. [N≡C–NH$^-$] for the reaction between **Cr-OMe-*p*-Cl** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(f). Summary of Data for the reaction between **Cr-OEt-H** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C

[CAN]/M	k_{obs}^{I} (Cr-OEt-H)/s^{-1}
0.025	16.94
0.035	18
0.050	20.6
0.063	23.7
0.075	24.3
0.088	26.4
0.100	29.5

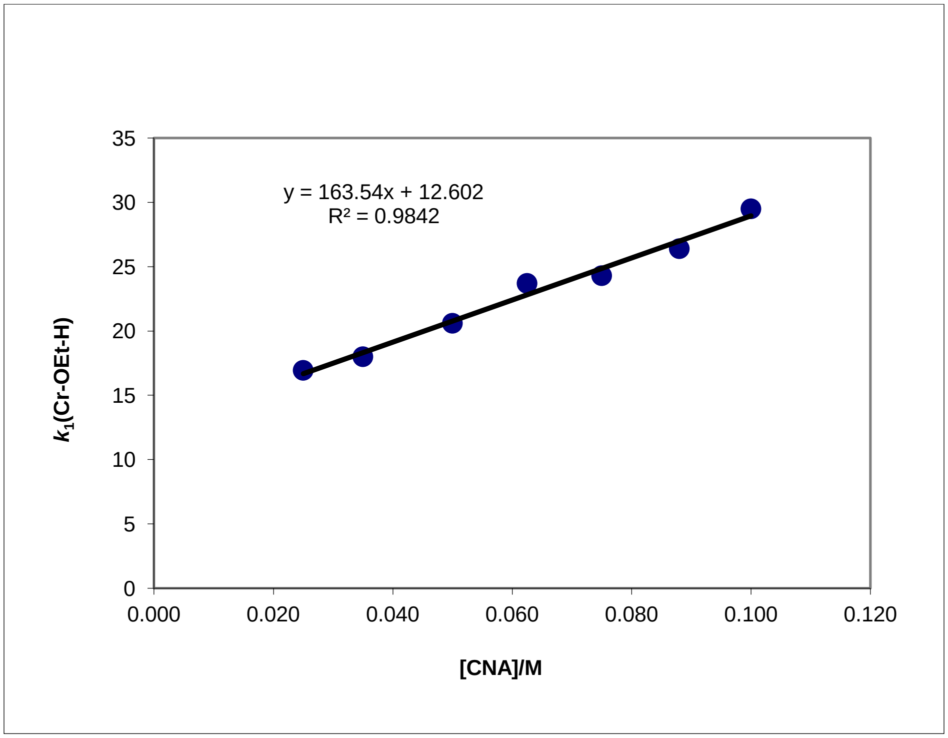

Figure S3(f). Plot of k_{obs}^{I} vs. [N≡C–NH$^-$] for the reaction between **Cr-OEt-H** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(g). Summary of Data for the reaction between **Cr-OEt-H** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C

[CAN]/M	$k_{obs}{}^{II}$(Cr-OEt-H)
0.0025	0.117
0.005	0.135
0.015	0.26
0.025	0.48
0.035	0.66
0.05	0.84
0.025	0.45
0.035	0.61
0.05	0.798

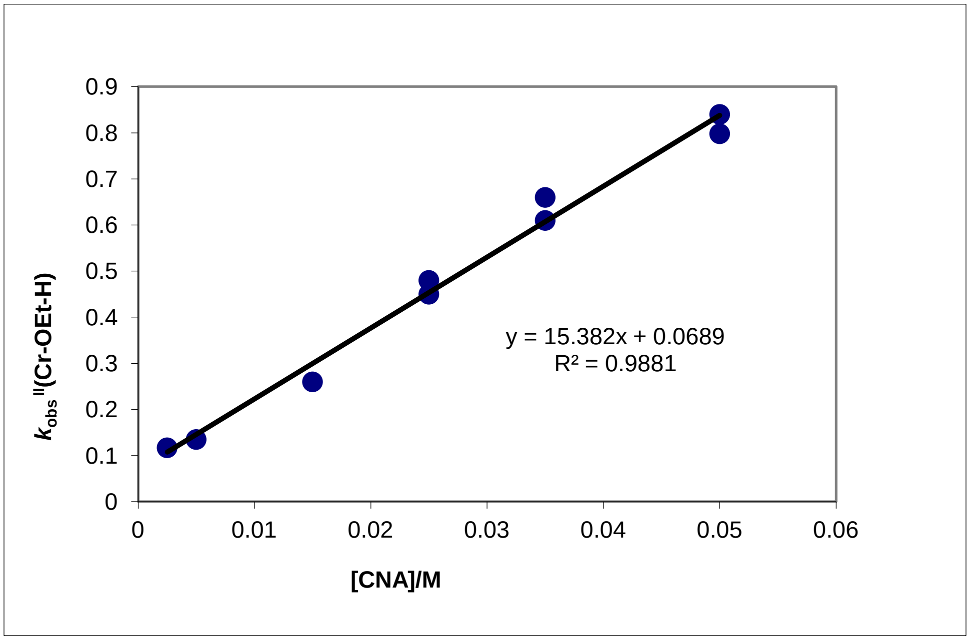

Figure S3(g). Plot of $k_{obs}{}^{II}$ vs. [N≡C–NH⁻] for the reaction between **Cr-OEt-H** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(h). Summary of Data for the reaction between **W-OMe-H** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C

[CAN]/M	k_{obs}^{I}/(**W-OMe-H**)/s^{-1}
0.025	38.850
0.035	51.500
0.050	71.000
0.063	76.000
0.075	89.000
0.088	104.000
0.100	112.000

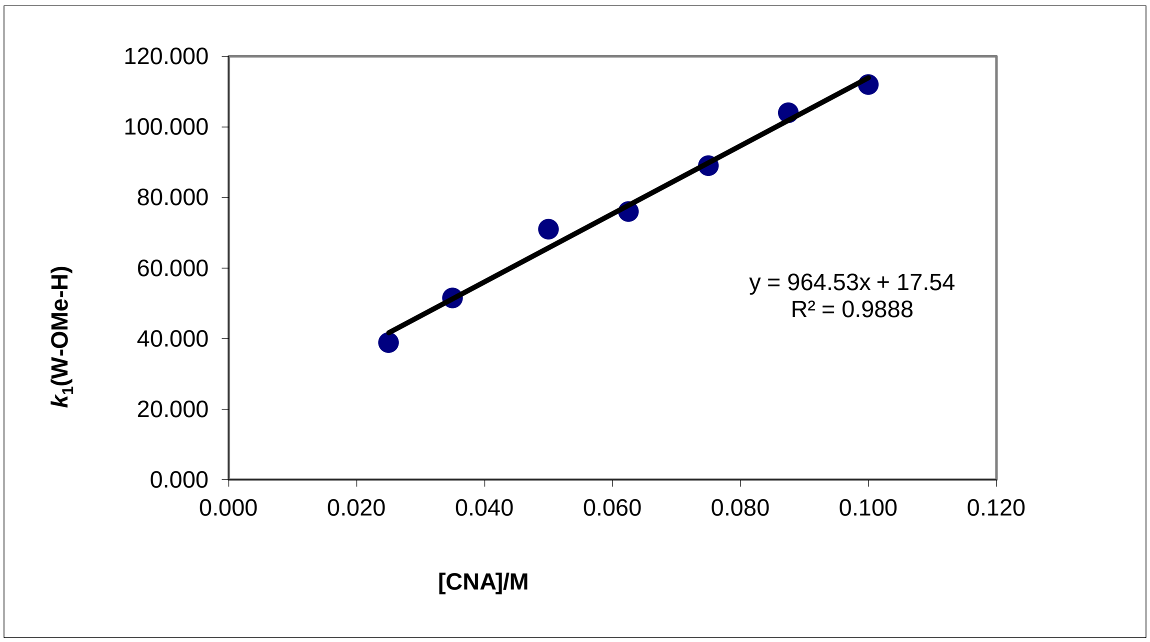

Figure S3(h). Plot of k_{obs}^{I} vs. [N≡C–NH⁻] for the reaction between **W-OMe-H** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(i). Summary of Data for the reaction between **W-OMe-H** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C

[CAN]/M	k_{obs}^{II}/(**W-OMe-H**)
0.025	6.090
0.035	8.500
0.050	10.900
0.063	15.000
0.075	17.000
0.088	19.400
0.100	22.000

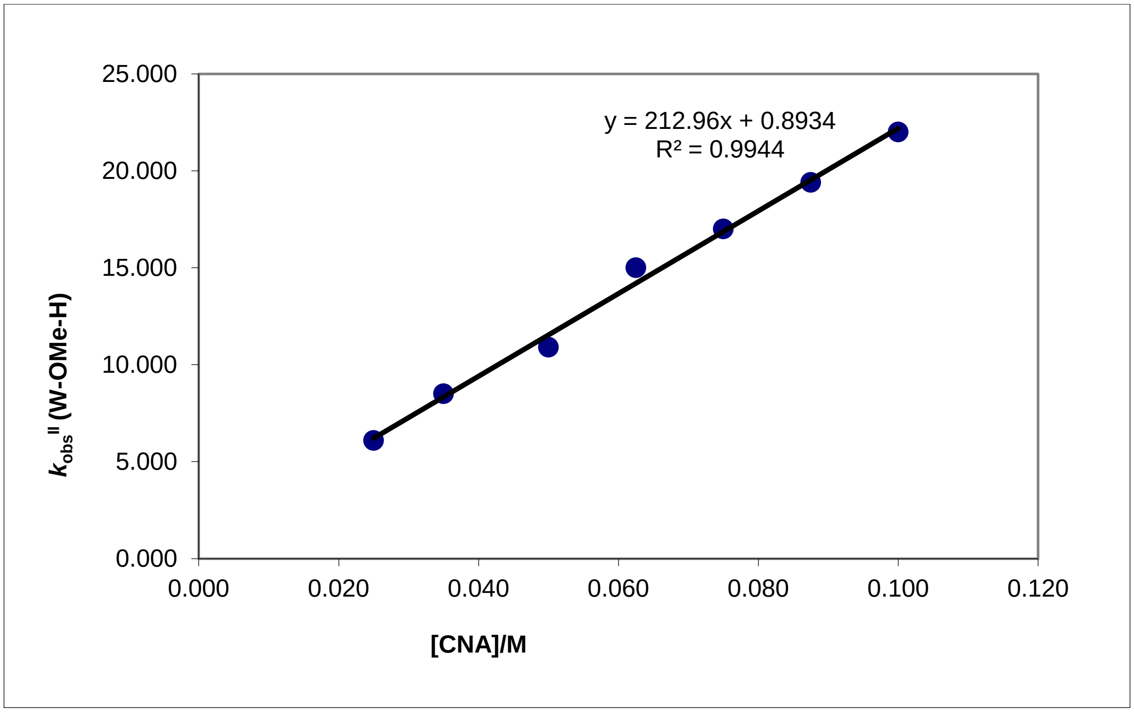

Figure S3(i). Plot of k_{obs}^{II} vs. [N≡C–NH$^-$] for the reaction between **W-OMe-H** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(j). Summary of Data for the reaction between **W-OEt-H** with N≡C–NH^{-} in 50%-MeCN-50% H_2O at 25 ^{0}C

[CAN]/M	k_{obs}^{I} /**W-OEt-H**
0.01	42
0.015	46
0.025	56
0.035	61.6
0.05	75

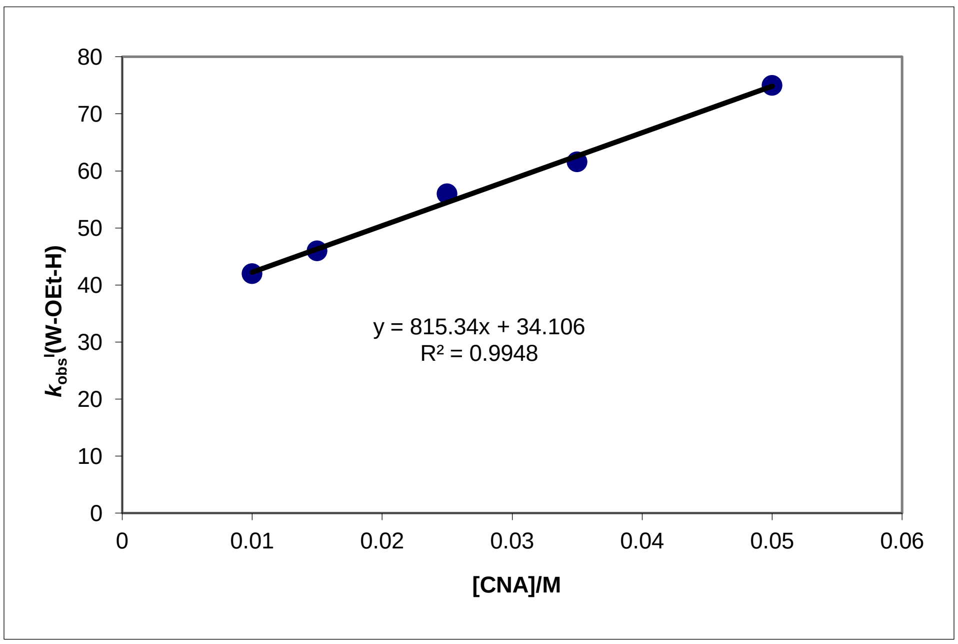

Figure S3(j). Plot of k_{obs}^{I} vs. [N≡C–NH^{-}] for the reaction between **W-OEt-H** with N≡C–NH^{-} in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(k). Summary of Data for the reaction between **W-OEt-H** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C

[CAN]/M	k_{obs}^{II} /W-OEt-H
0.0025	0.137
0.005	0.22
0.015	0.58
0.025	0.889
0.035	1.29

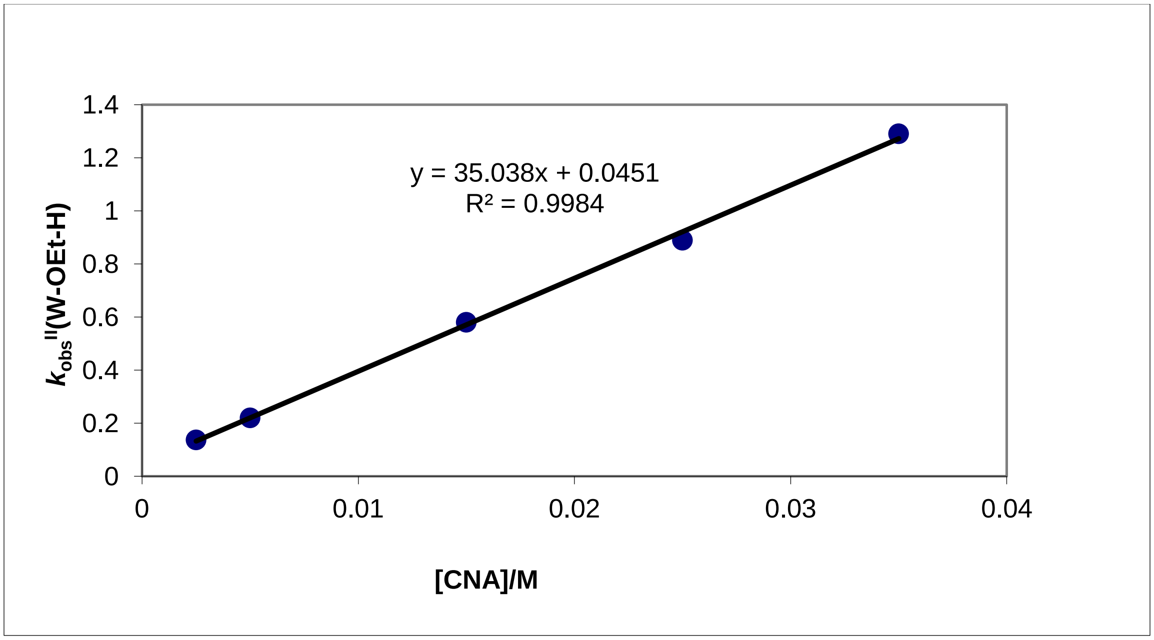

Figure S3(k). Plot of k_{obs}^{II} vs. [N≡C–NH$^-$] for the reaction between **W-OEt-H** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(l). Summary of substituent constants and rate constants (k_1)for the reactions of N≡C-NH$^-$ with **Cr-OMe-Z** in 50% MeCN-50% Water (v/v) at 25 °C

Cl	0.23	3.35	2234.00
F	0.06	2.98	955.20
H	0	2.72	525.10
Me	-0.17		
OMe	-0.27	1.95	89.27
NMe2	-0.83	0.21	1.61
SPW			

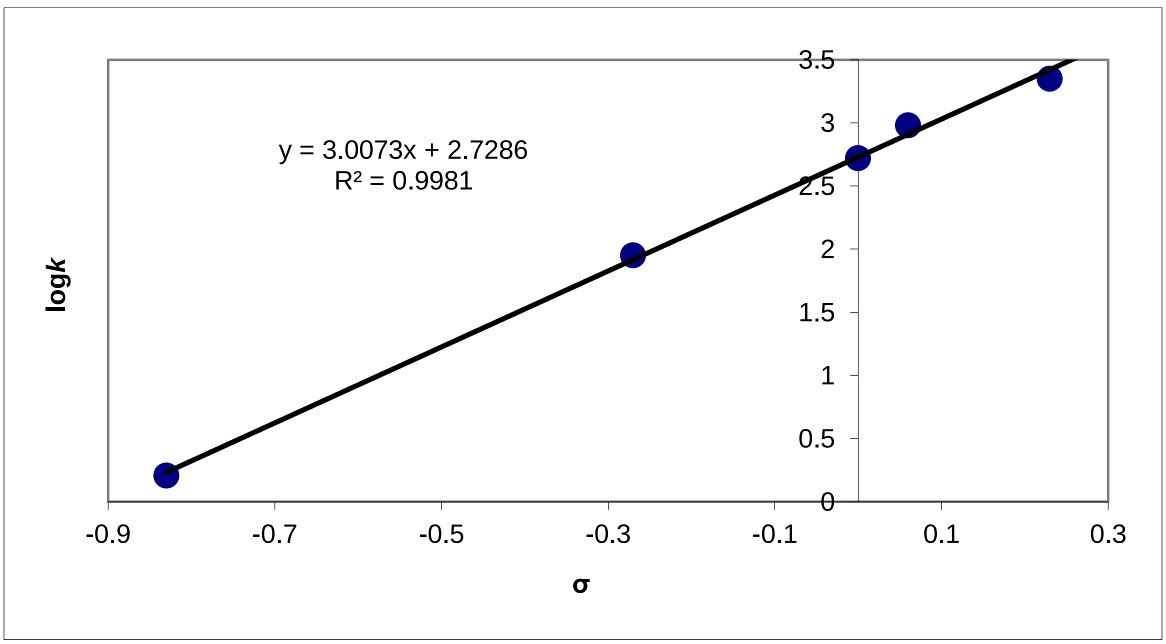

Figure S3(l) . Hammette plot of k_1(M^{-1}s^{-1}) for the reactions of N≡C-NH$^-$ with **Cr-OMe-Z** in 50% MeCN-50% Water (v/v) at 25 °C

Table S3(m). Summary of Data for the reaction between **W-OEt-H** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C

[CAN]/M	$k_{obs}{}^{II}$/s^{-1}(F)
0.01	0.90
0.02	1.68
0.03	3.60
0.04	4.50
0.05	7.60
0.10	15.20

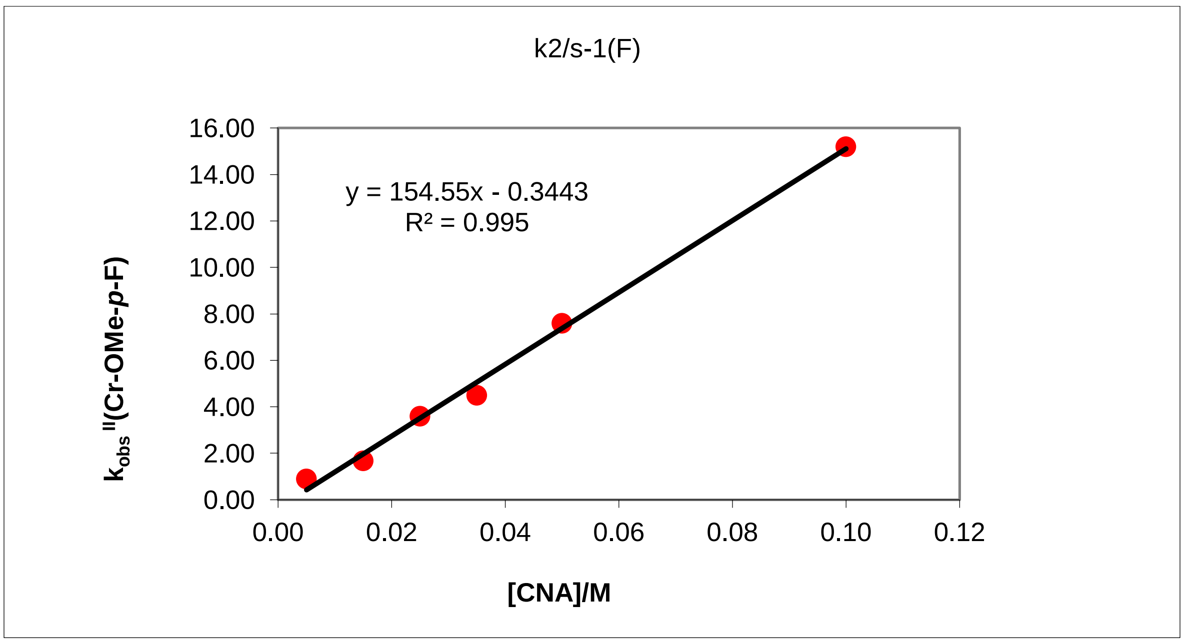

Figure S3(m). Plot of $k_{obs}{}^{II}$ vs. [N≡C–NH$^-$] for the reaction between **Cr-OMe-*p*-F** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(n). Summary of Data for the reaction between **W-OEt-H** with N≡C–NH^{-} in 50%-MeCN-50% H_2O at 25 ^{0}C

[CAN]/M	$k_{obs}{}^{II}$ /s^{-1}(Cl!)
0.01	1.85
0.02	4.68
0.03	6.72
0.04	10.20
0.05	15.90
0.10	30.90

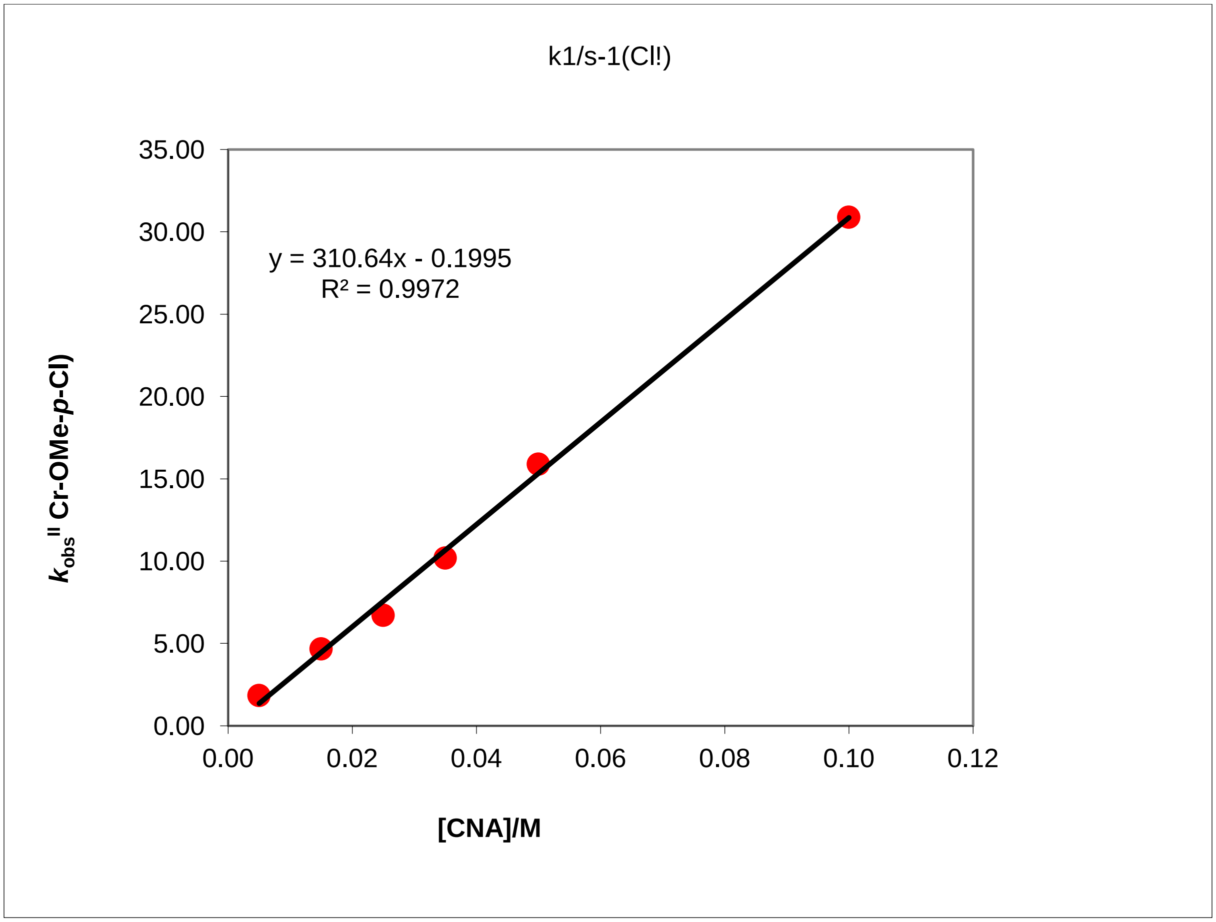

Figure S3(n). Plot of $k_{obs}{}^{II}$ vs. [N≡C–NH^{-}] for the reaction between **Cr-OMe-*p*-Cl** with N≡C–NH^{-} in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(o). Summary of Data for the reaction between **Cr-OMe-H** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C

[CAN]/M	k_{obs}^{II} /s^{-1} (Cr-OMe-H)
0.03	3.10
0.04	4.50
0.05	6.70
0.06	8.26
0.08	8.80
0.09	10.29
0.10	11.89

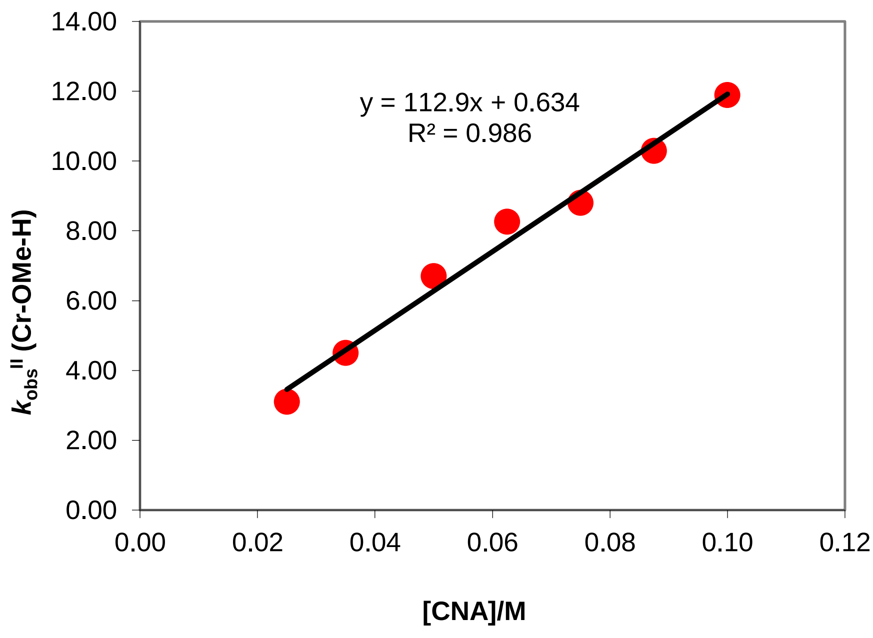

Figure S3(o). Plot of k_{obs}^{II} vs. [N≡C–NH⁻] for the reaction between **Cr-OMe-H** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S3(p). Summary of Data for the reaction between **Cr-OMe-*p*-OMe** with N≡C–NH^{-} in 50%-MeCN-50% H_2O at 25 ^{0}C

[CAN]/M	k_{obs}^{II} /s^{-1} (Cr-OMe-OMe)
0.01	0.02
0.02	0.17
0.03	0.22
0.04	0.39
0.05	0.52
0.08	0.80

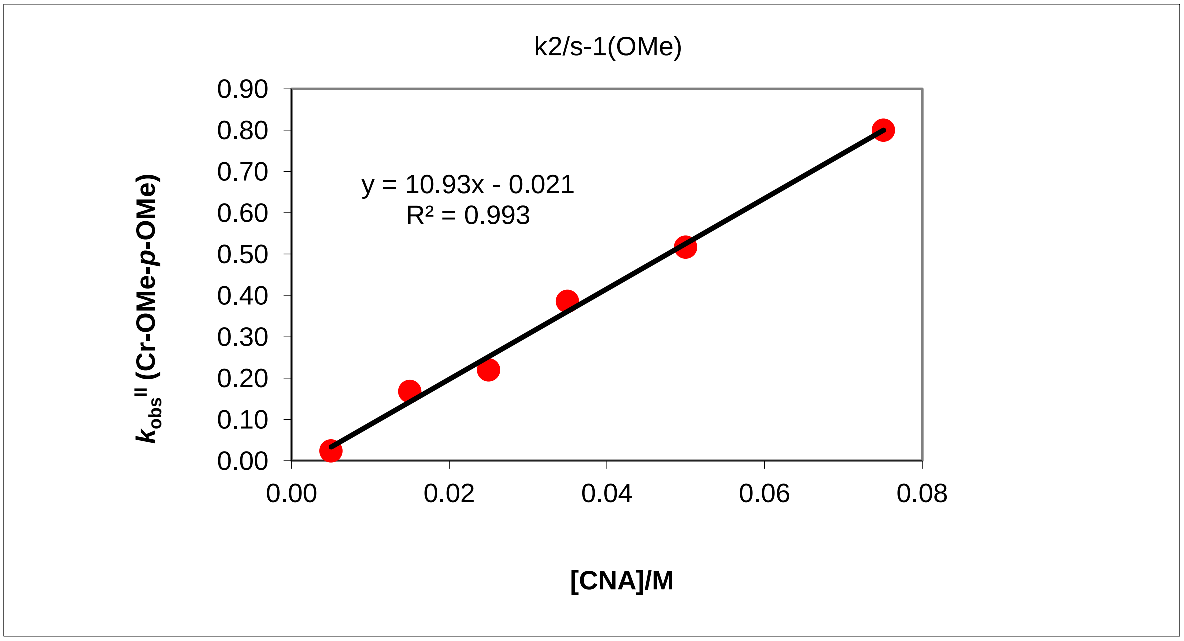

Figure S3(p). Plot of k_{obs}^{II} vs. [N≡C–NH^{-}] for the reaction between **Cr-OMe-*p*-OMe** with N≡C–NH^{-} in 50%-MeCN-50% H_2O at 25 ^{0}C

Table S3(q). Summary of substituent constants and rate constants (k_2) for the reactions of N≡C-NH$^-$ with **Cr-OMe-Z** in 50% MeCN-50% Water (v/v) at 25 °C

	σ	log(k_2)	k_2/ $M^{-1}s^{-1}$
Cl	0.23	2.492	310.64
F	0.06	2.189	154.55
H	0	2.053	112.90
OMe	-0.27	1.039	10.93

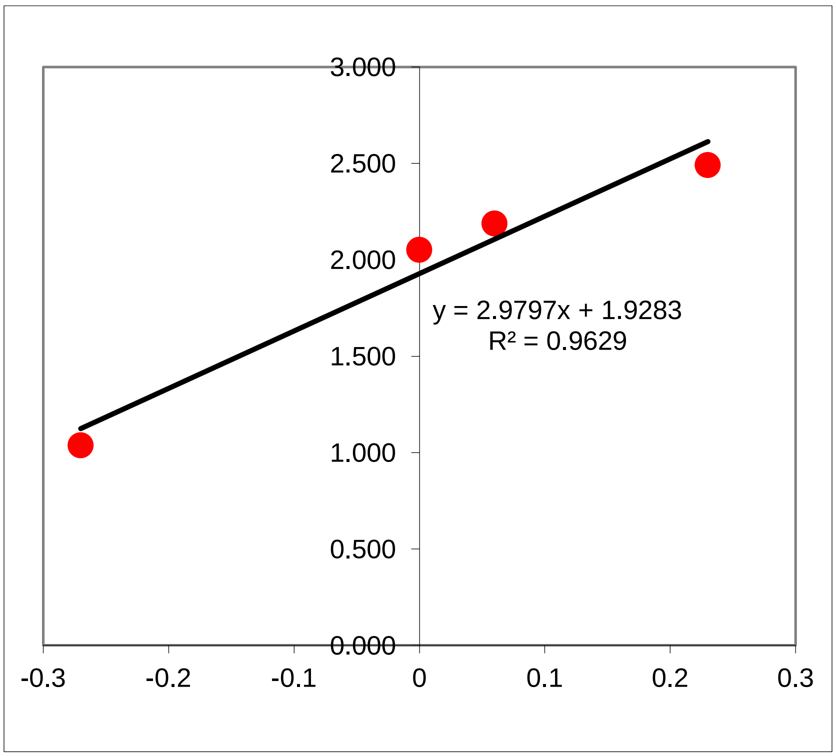

Figure S3(q) . Hammette plot of k_2 ($M^{-1}s^{-1}$) for the reactions of N≡C-NH$^-$ with **Cr-OMe-Z** in 50% MeCN-50% Water (v/v) at 25 °C

Table S4(a). Summary of Data for the reaction between **Cr-SMe-*p*-NMe₂** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	k_{obs}^{I} /s^{-1}
0.025	0.043
0.035	0.059
0.050	
0.063	0.105
0.075	0.125
0.088	0.144
0.100	0.167

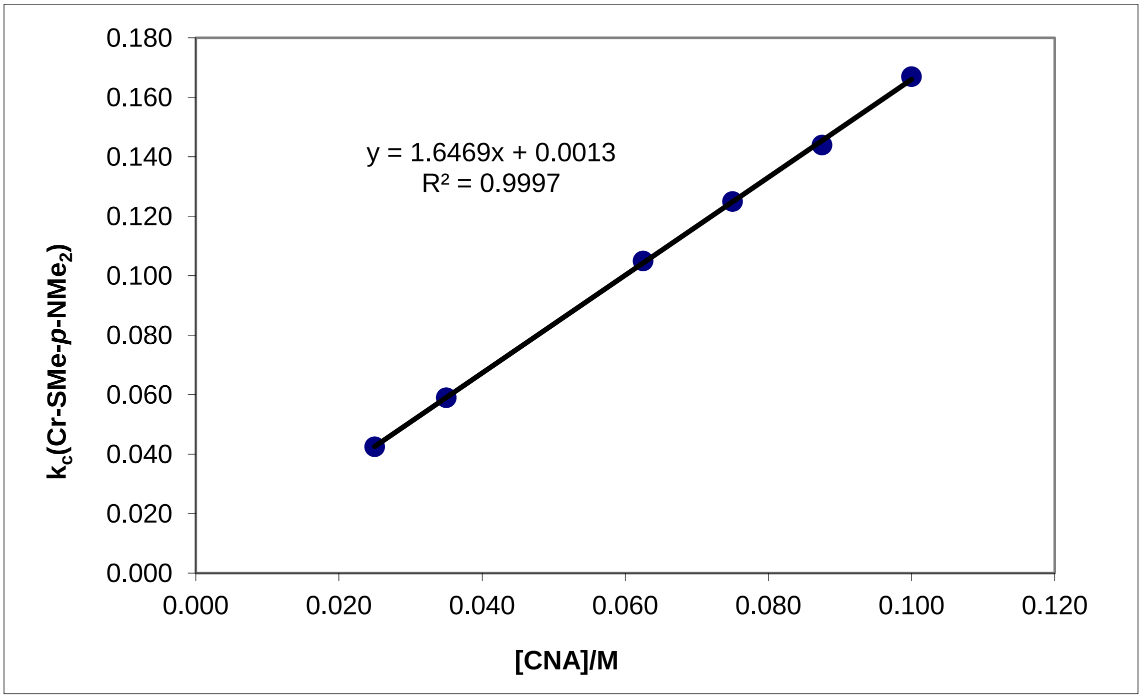

Figure S4(a). Plot of k_{obs}^{I} vs. [N≡C–NH⁻] for the reaction between **Cr-SMe-*p*-NMe₂** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S4(b). Summary of Data for the reaction between **Cr-SMe-*p*-OMe** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	$k_{obs}{}^{I}$ /s^{-1}
0.025	0.220
0.035	0.290
0.050	
0.063	0.385
0.075	0.485
0.088	0.547
0.100	0.600

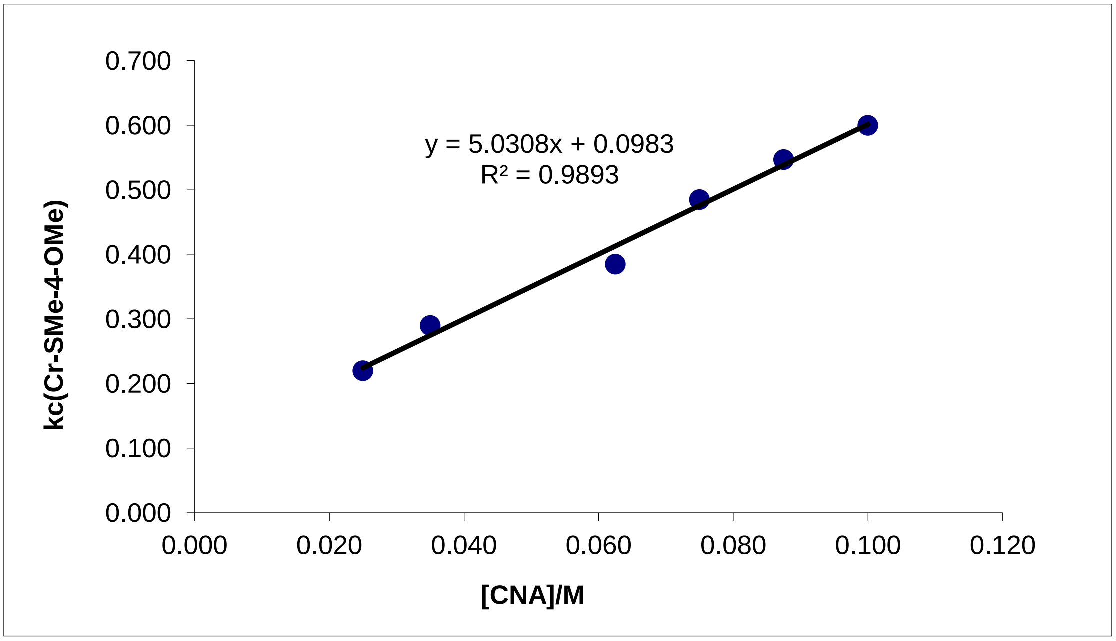

Figure S4(b). Plot of $k_{obs}{}^{I}$ vs. [N≡C–NH$^-$] for the reaction between **Cr-SMe-*p*-OMe** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S4(c). Summary of Data for the reaction between **Cr-SMe-*p*-Me** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	$k_{obs}{}^{I}$ /s^{-1}
0.025	0.260
0.035	0.335
0.050	
0.063	0.519
0.075	0.592
0.088	0.675
0.100	0.768

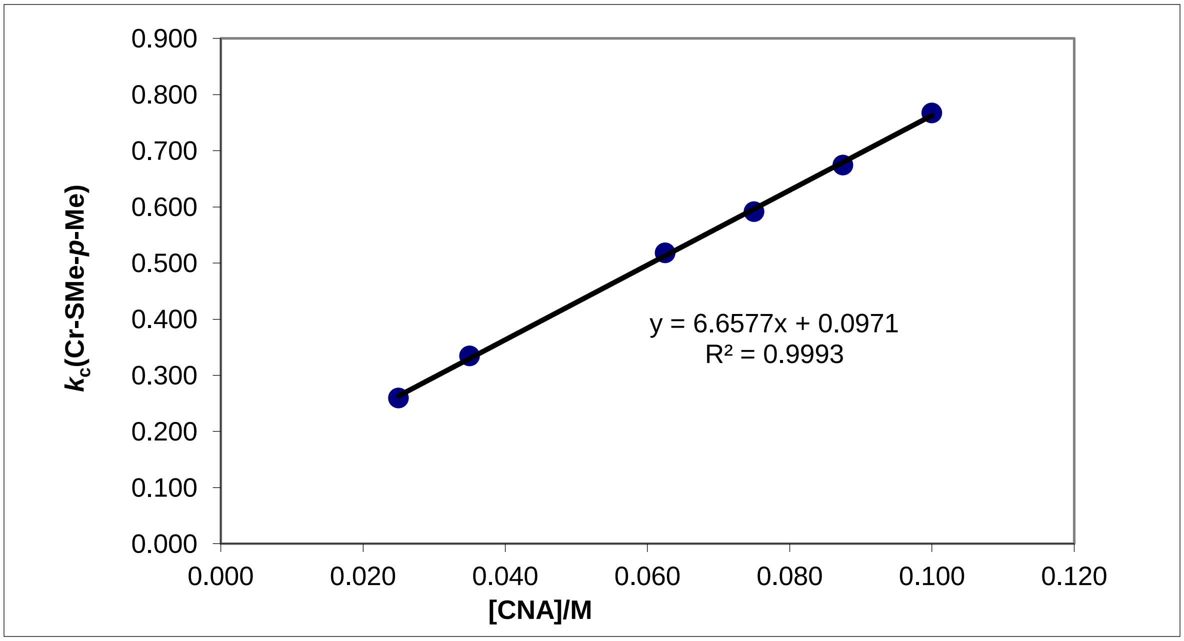

Figure S4(c). Plot of $k_{obs}{}^{I}$ vs. [N≡C–NH⁻] for the reaction between **Cr-SMe-*p*-Me** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S4(d). Summary of Data for the reaction between **Cr-SMe-H** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	$k_{obs}{}^{I}$ /s^{-1}
0.0025	0.039
0.005	0.0685
0.015	0.169
0.025	0.265
0.035	0.345
0.05	0.485

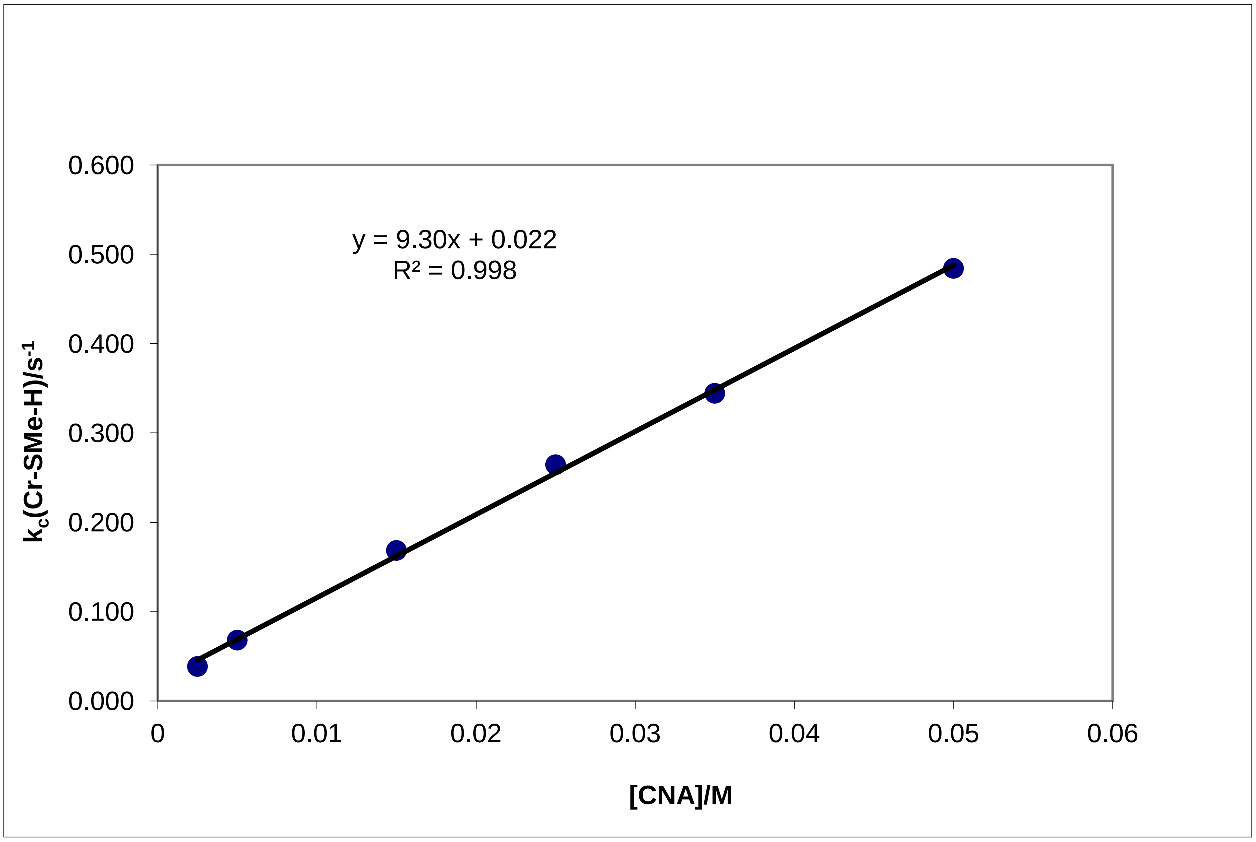

Figure S4(d). Plot of $k_{obs}{}^{I}$ vs. [N≡C–NH$^-$]for the reaction between **Cr-SMe-H** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S4(e). Summary of Data for the reaction between **W-SMe-H** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	$k_{obs}{}^{I}$ /s^{-1}
0.0025	0.148
0.005	0.265
0.015	0.679
0.025	1.073
0.035	1.446
0.05	2.035

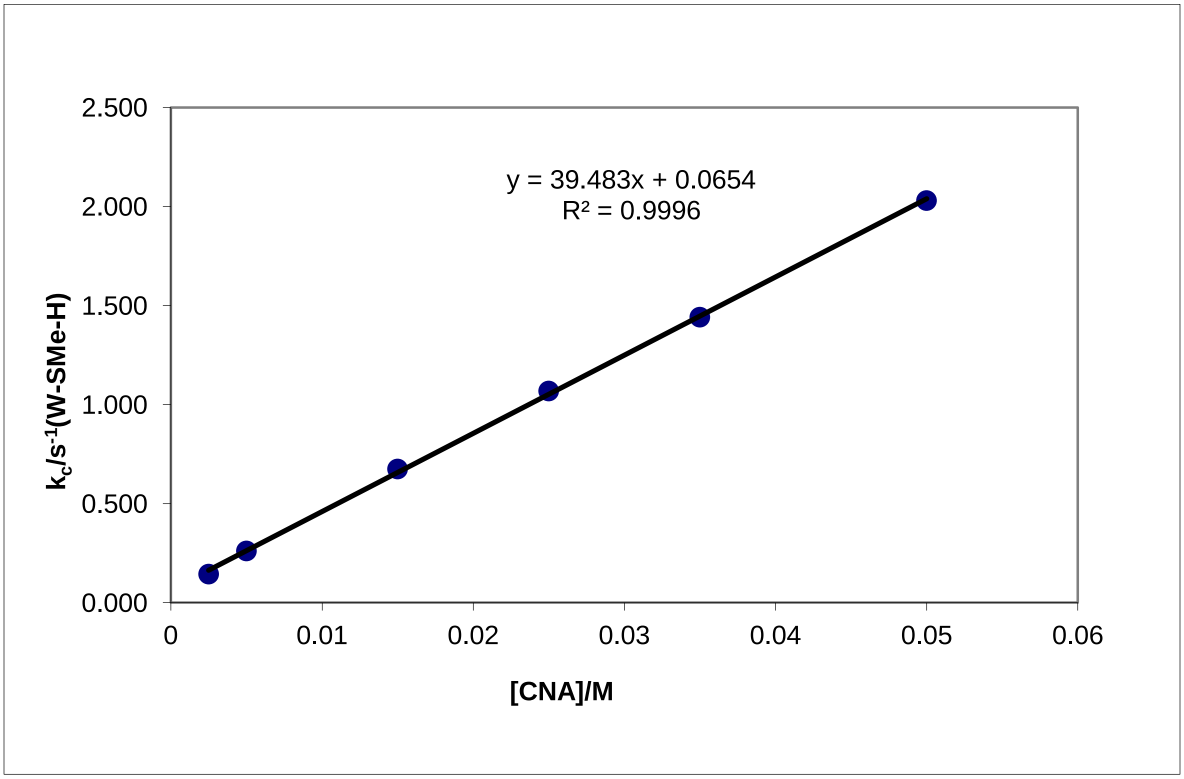

Figure S4(e). Plot of $k_{obs}{}^{I}$ vs. [N≡C–NH⁻] for the reaction between **W-SMe-H** with N≡C–NH⁻ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S4(f). Summary of Data for the reaction between **Cr-SMe-*p*-F** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	k_{obs}^{I} /s^{-1}
0.025	0.367
0.035	0.469
0.050	0.762
0.063	0.932
0.075	1.155
0.088	1.332
0.100	1.600

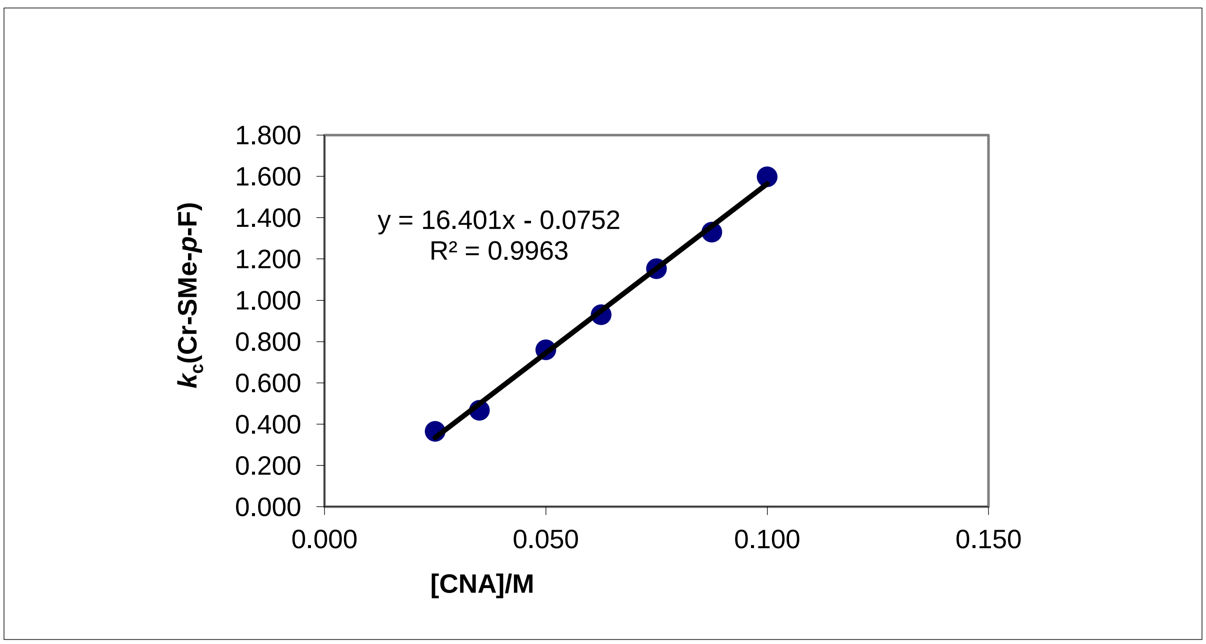

Figure S4(f). Plot of k_{obs}^{I} vs. [N≡C–NH$^-$]for the reaction between Cr-SMe-*p*-F with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S4(g). Summary of Data for the reaction between **Cr-SMe-*m*-Cl** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	k_{obs}^{I} /s^{-1}
0.025	0.685
0.035	0.850
0.050	
0.063	1.420
0.075	1.610
0.088	1.920
0.100	2.200

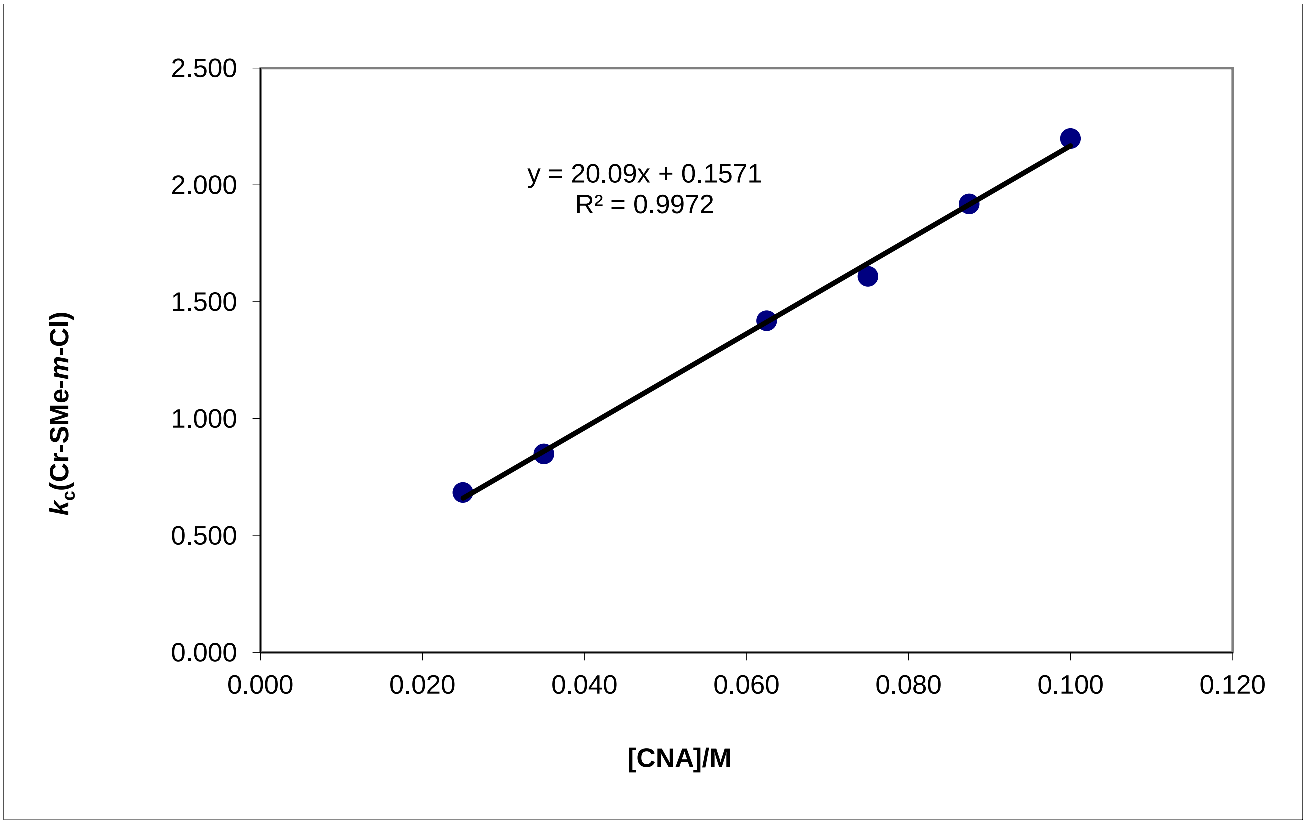

Figure S4(g). Plot of k_{obs}^{I} vs. [N≡C–NH$^-$] for the reaction between **Cr-SMe-*m*-Cl** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S4(h). Summary of Data for the reaction between Cr-SMe-*p*-Cl with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	k_{obs}^{I} /s^{-1}
0.025	0.578
0.035	0.769
0.050	1.091
0.063	1.179
0.075	1.440
0.088	1.640
0.100	1.920

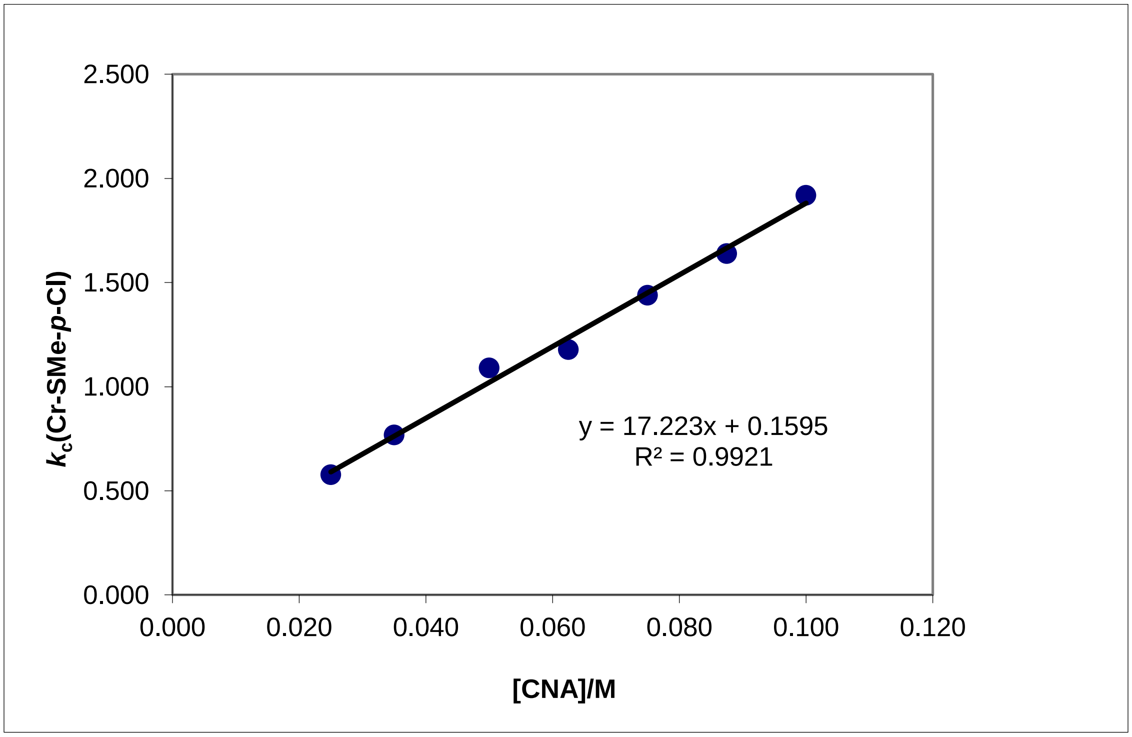

Figure S4(h). Plot of k_{obs}^{I} vs. [N≡C–NH$^-$]for the reaction between **Cr-SMe-*p*-Cl** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

Table S4(i). Summary of Data for the reaction between **Cr-SMe-*p*-CF$_3$** with N≡C–NH$^-$ in 50%-MeCN-50% H_2O at 25 ^{0}C.

[CAN]/M	k_{obs}^{I} /s^{-1}
0.025	0.784
0.035	1.108
0.050	
0.063	1.878
0.075	2.277
0.088	2.657
0.100	3.067

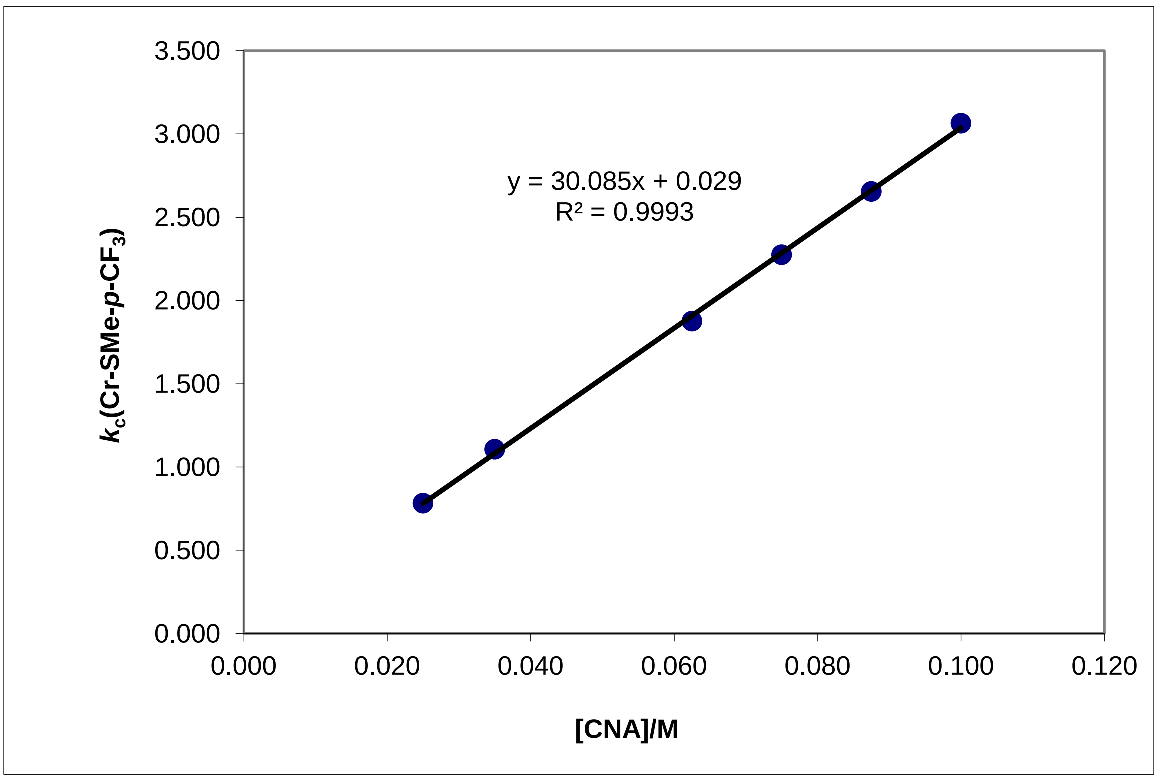

Figure S4(i). Plot of k_{obs}^{I} vs. [N≡C–NH$^-$]for the reaction between **Cr-SMe-*p*-CF$_3$** with N≡C–NH$^-$ in 50%-MeCN- 50% H_2O at 25 ^{0}C.

Table S4(j). Summary of substituent constants and rate constants for the reactions of N≡C-NH⁻ with **Cr-SMe-Z** in 50% MeCN-50% Water (v/v) at 25 °C

Substituent	σ	log(k_1)	k_1/$M^{-1}s^{-1}$
CF3	0.540	1.478	30.08
Cl(3)	0.370	1.303	20.09
Cl	0.230	1.236	17.22
F	0.060	1.215	16.40
H	0.000	0.968	9.30
Me	-0.170	0.823	6.66
Ome	-0.270	0.702	5.03
NMe2	-0.830	0.217	1.65

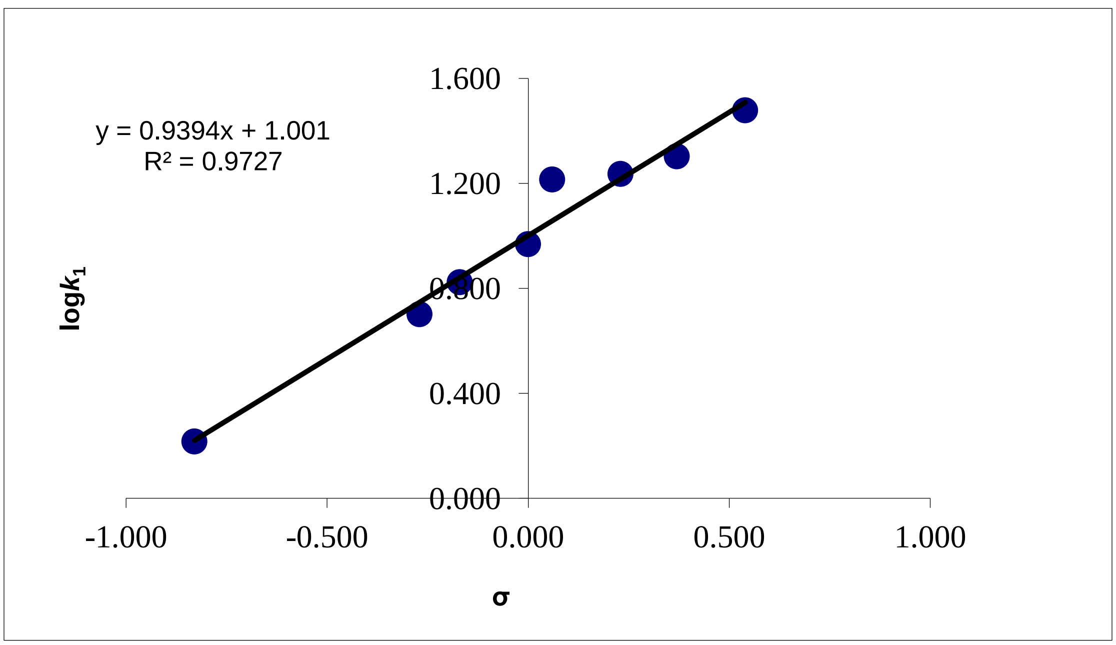

Figure S4(j) . Hammette plot for the reactions of N≡C-NH⁻ with **Cr-SMe-Z** in 50% MeCN-50% Water (v/v) at 25 °C